



Lithium ion conductive $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ based inorganic–organic composite separator with enhanced thermal stability and excellent electrochemical performances in 5 V lithium ion batteries

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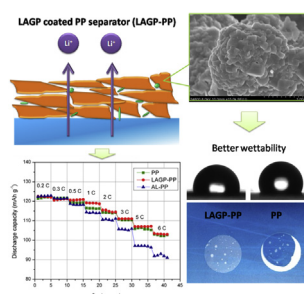
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HIGHLIGHTS

- Li-ion conductive $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ is used as an active coating layer.
- Higher ion conductivity than the inert inorganic coating layer is obtained.
- The composite separator owns enhanced thermal stability and wettability.
- The coin cells show excellent C-rate capacity and cyclability.

GRAPHICAL ABSTRACT



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ABSTRACT

Since 5 V lithium ion batteries have attracted more and more attentions and are deemed to be an important tendency in the future, the matched design of the separators has also become a necessary and significant work. In this work, the lithium ionic conducting glass ceramic $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ -polypropylene (PP) based inorganic–organic composite separator (LAGP-PP) is prepared. Compared with the pristine PP separator, the LAGP-PP separator owns enhanced thermal stability and wettability. Meanwhile, the LAGP-PP separator shows higher ion conductivity than the traditional Al_2O_3 coated PP separator due to the more facile lithium ion diffusion channels in the coating layer. The superior C-rate capacity and cyclability in the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ based 5 V lithium ion batteries indicate that the LAGP-PP separator is a good alternative for the traditional inert inorganic ceramic coated polyolefin separators and is a kind of promising candidate separator for the high voltage lithium ion batteries.

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1. Introduction

Applications in (hybrid) electric vehicles and energy storage have challenged the development of lithium ion batteries [1].

Developing the advanced and high energy/high power density lithium ion batteries is one of the most important and attractive topics in modern electrochemistry [2]. Thereinto, 5 V lithium-ion batteries have attracted a lot of attention due to higher operating voltage and substantially increased energy density compared with the present 4 V ones [3]. As an important component of the high voltage lithium ion batteries, separators are required to own enough chemical and thermal stability to ensure the safety and

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cycling performances of the batteries. However, less attention has been paid to the designation of the separators for the 5 V-class high voltage lithium ion batteries.

So far, polyolefin based separators have been most widely used ones in the lithium ion batteries due to their low cost and proper mechanical strength etc. However, the main drawbacks for this kind of separators lie in intrinsic hydrophobicity and poor thermal stability. The hydrophobic property and low surface energy lead to weak interaction between the separator and the high polar liquid electrolyte and poor wettability, which would bring serious disadvantages in the manufacturing costs and battery performances [4]. The melting point of the polyolefin materials only ranges from 135 to 165 °C. In the case of battery heating, separators tend to shrink or break, leading to internal short circuit, thermal runaway and even explosion, which seriously threatens the safety of the batteries. Besides, in the high voltage lithium ion batteries, polyolefin separators also face the risk of being oxidized, which would deteriorate the mechanical strength of the separators and battery performances. Therefore, separators are required to own higher chemical stability and enhanced antioxidant capacity.

To overcome these above problems, introducing inorganic coating layer is considered to be an ideal solution. Firstly, the inorganic nanoparticles could provide enhanced wettability [5–7]. Secondly, the inorganic coating layers usually own excellent heat resistance, which could give separator better thermal stability [8,9]. Furthermore, the superior flame retardant properties of inorganic nanoparticles could provide higher security for the lithium ion batteries. Finally, the inorganic coating layer could protect the polymer matrix from oxidation effectively [10]. The most widely used inorganic ceramics include SiO_2 , Al_2O_3 , ZrO_2 , NaY zeolite, TiO_2 and so on [11–15]. However, due to the increased conduction resistance for the lithium ions in the coating layers, introduction of the inorganic coating layers usually results in decreased ion conductivities and poor C-rate capacity [15,16].

$\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ (LAGP) is a kind of lithium ionic conducting glass ceramic with high bulk ion conductivity (about $10^{-4} \text{ S cm}^{-1}$), which has been used as the inorganic solid electrolyte in the lithium ion batteries [17,18]. Herein, the authors introduced LAGP onto the polypropylene (PP) separator to achieve a kind of high wettability, high chemical/thermal stability and high mechanical strength composite separator. The separator is expected to alleviate the ion conductivity decrease induced by the introduction of the inert inorganic coatings, which is considered to be a more suitable candidate for the application in the high voltage high power/energy density lithium ion batteries in terms of battery safety and C-rate capacity. The physical and electrochemical performances of the LAGP coated PP separator were explored.

2. Experimental

2.1. Fabrication of lithium-ion conducting LAGP particles

A conventional melting-quenching method was used to prepare the LAGP particles [19]. Stoichiometric amounts of lithium carbonate (Li_2CO_3 , A.R.), aluminum hydroxide ($\text{Al}(\text{OH})_3$, A.R.), germanium oxide (GeO_2 , 99.99%) and ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$, A.R.) were thoroughly mixed by the planetary ball milling. Then the mixture was heated at 700 °C for 2 h in an alumina crucible. The obtained powders were reground and then sintered at 1350 °C for 2 h. Finally, the product was shifted to a furnace at 500 °C for 2 h for annealing and then cooled naturally.

2.2. Preparation of the LAGP coated PP separator (LAGP-PP) and the Al_2O_3 coated PP separator (AL-PP)

Dissolved 1 g polyvinylidene fluoride (PVDF, HSV900, Arkema) in 40 g N-methyl-2-pyrrolidone (NMP), followed by dispersing 9 g LAGP into the solution to form the 20 wt% coating solution. Then the coating solution was uniformly spread onto the cleaned PP separator (Donghang Optoelectronics Technology Co., Ltd., China, 20 μm) using an applicator with a clearance of 10 μm . Subsequently, it was transferred into the 60 °C oven for 6 h for solvent evaporation. Finally, the composite separator (LAGP-PP) was obtained. For the AL-PP, similar preparation process was used with replacing the LAGP with Al_2O_3 (50 nm, Aladdin).

2.3. Characterization of the PP separator and the composite separators

The X-ray powder diffraction (XRD) of the LAGP was operated on an AXSD8 Advance diffractometer with Cu K α radiation. The scan range was from 10° to 90°. The morphologies of the LAGP and the separators were characterized by field emission scanning electron microscopy (FESEM, S-4800, Hitachi, Japan) after applying a gold coating. Gurley value was determined on a home-made instrument with dry separator. For this test, the time for 30 ml air to pass through a fix area (0.79 cm^2) under certain pressure (0.02 MPa) was

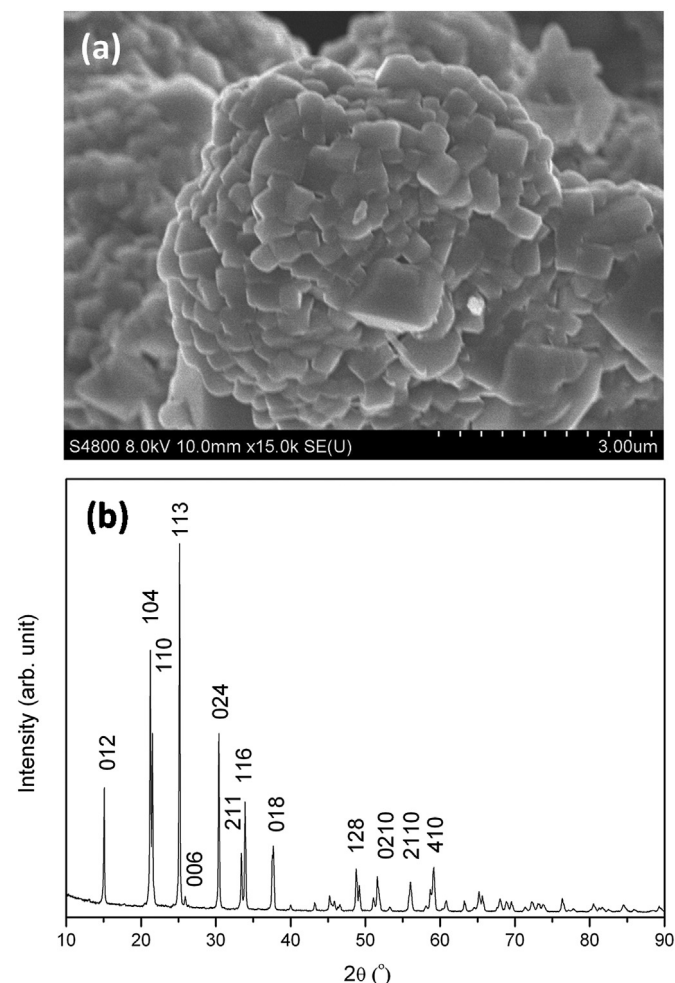


Fig. 1. (a) SEM image of the LAGP particle. (b) XRD pattern of the LAGP particle recorded at room temperature.

measured. The water contact angle on the separator was determined by the contact angle measurement system (Dataphysics, OCA20, Germany) at 25 °C.

The electrolyte uptake (U) was obtained by immersing the separators into liquid electrolyte until saturated, and then the weight change was determined. It is calculated as the eq. (1):

$$U(\%) = 100 \times (M - M_0)/M_0 \quad (1)$$

where M_0 and M represent the weight of the dry and wetted separator, respectively.

The impedance was determined on the electrochemical workstation system (CHI660e, China). The bulk impedance (R_b) was obtained with the assembly of stainless steel (SS)/separator/SS. The ion conductivity (σ) could be calculated by the eq. (2):

$$\sigma = d/(R_b \times A) \quad (2)$$

where d and A are the thickness and the effective area of the separator, respectively.

The charge/discharge cycling performances were measured on a cell testing system (LAND CT2001A, China) between 3 V and 5 V under different current rates. The coin cells containing $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode and lithium anode were used. The cathode contains the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, super P and PVDF with a mass ratio of 8:1.5:0.5 (wt:wt:wt). The interfacial resistance before and after the

cycling process were determined on the Autolab PGSTAT302N electrochemical workstation (Metrohm, Switzerland).

3. Results and discussion

Fig. 1a shows the SEM photograph of the LAGP particles. The size of the primary particle ranges from 0.3 to 0.6 μm . The particle size of the LAGP is about 10–20 μm (Fig. 2). The XRD pattern of the LAGP is given in Fig. 1b. The pattern shows only broad bands, indicating the glass nature of the LAGP. The NASICON-type phases are obtained in LAGP particles, suggesting that a solid solution as Al^{3+} ions replacing the Ge^{4+} is formed. According to previous reports [19], the NASICON-type structure could provide suitable tunnels for lithium ion migration in the LAGP particles.

Fig. 2 shows the SEM images of the LAGP-PP, AL-PP and the commercialized PP separator. As displayed, the commercialized PP separator has needle-like pores with the average pore size being about 2 μm , which is prepared via the traditional melt spinning cold stretching method. The thickness of the PP separator is 20 μm . For the coated composite separator, the coating layer is about 5 μm . The LAGP-PP separator has larger inorganic particle size than the AL-PP one, which is used as a comparison.

Gurley value is used to quantitatively characterize the pore structure of the separators and the state of pore blocking of the coating layers. Generally, the high Gurley value corresponds to a long tortuous path for air permeability [20]. As shown in Table 1, The Gurley value of the pristine PP separator is 116 s 100 ml^{-1}

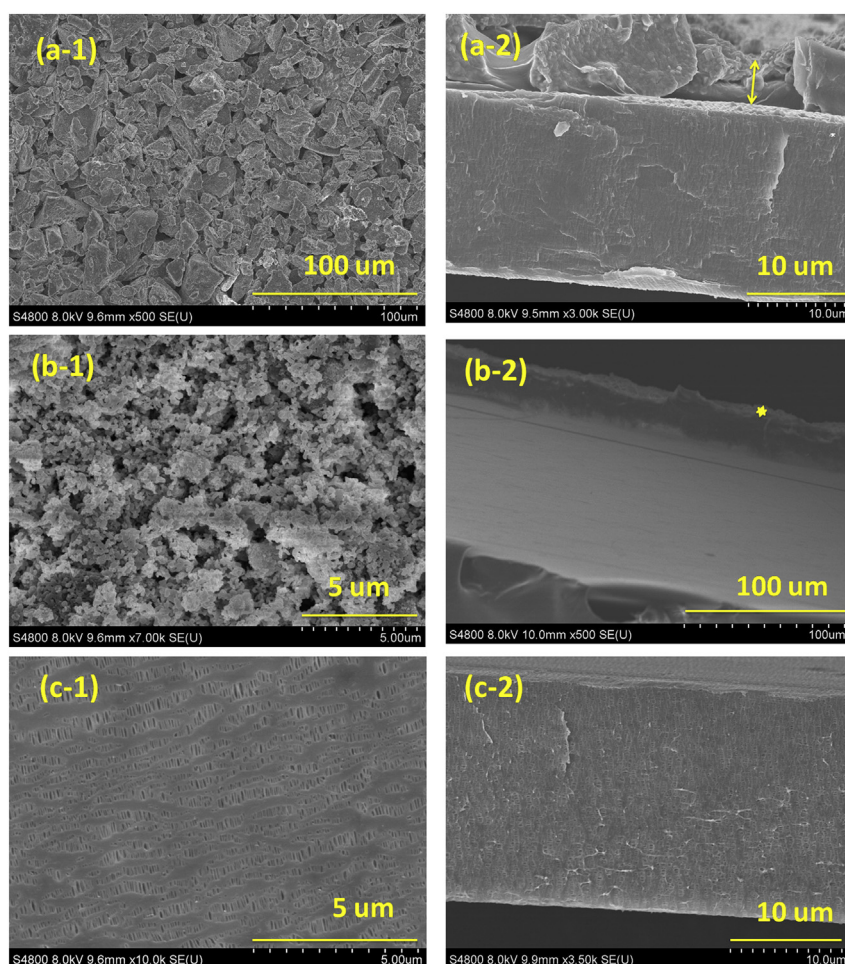


Fig. 2. The surface (left) and cross-section (right) morphologies of the (a) LAGP-PP, (b) AL-PP and (c) the commercial PP separator.

Table 1
Comparison of the basic properties of the PP, AL-PP, LAGP-PP separators.

Separator code	Thickness (μm)	Gurley value (sec 100 ml^{-1})	Contact angle ($^\circ$)	Uptake (%)
PP	20	116	114	121
AL-PP	25	131	92	135
LAGP-PP	25	142	100	132

(0.02 MPa, 0.79 cm^2). Gurley value increases when the ceramic coating layer is introduced. Meanwhile, the Gurley value of the LAGP-PP separator is higher than that of the AL-PP one, suggesting that the interstitial voids formed between the LAGP particles in the coating layer are less. This is because larger LAGP particles are used. The formed voids in the coating layer would largely influence the mobility and transportation of the lithium ions, which would be discussed later.

The thermal resistance of separators has a great relationship with battery safety, since severe shrinkage of separators caused by the heat generated during battery cycling process and especially under high power output would cause short circuit of the batteries [21]. The thermal stability of the separators is evaluated by observing the thermal shrinkage when separators are deposited on the oven at different temperatures for 1 h continuously (Fig. 3a). The pristine PP separator shows more obvious shrinkage and is totally melted down when the temperature is 160°C . This is because the melting point of PP is $160\text{--}165^\circ\text{C}$. The inorganic LAGP coated PP separator owns better thermal stability, implying that the introduction of the inorganic LAGP particles is effective for improving the thermal performances of the separators.

The wettability of the separators is further evaluated and the water contact angle is determined. As depicted in Fig. 3b, compared with the 114° for the PP separator, the LAGP-PP separator shows a

lower contact angle of 100° , suggesting that the introduction of the inorganic particles makes the composite separator to be more hydrophilic. This result implies that the composite separator owns a good surface wettability with the polar solvent. The electrolyte wettability is further characterized by adding a drop of liquid electrolyte on the surface of the separators. As can be seen in Fig. 3c, the LAGP-PP could be quickly wetted. The fast and uniform wetting of liquid electrolyte on the LAGP-PP is deemed to be favorable for higher productivity and improved cycling performances of the lithium ion batteries, which is a more serious concern for the large-size batteries for the application in (hybrid) electric vehicles and energy storage [6]. Since the coating layer could also absorb a certain amount of liquid electrolyte, the total uptake of the ceramic coated separator increases (Table 1, 132% for LAGP-PP separator and 135% for AL-PP separator).

The electrochemical performances of the LAGP-PP, AL-PP and PP separator are compared in detail. Firstly, the bulk impedance of the separators was determined and the ion conductivity at 25°C was calculated. As shown in Fig. 4a, the Nyquist plots of the separators are straight lines, suggesting that the current carriers are ions and the total conductivity is the ion conductivity [22]. The intercept of the straight line with the Z' axis is the bulk impedance. When the inorganic coating layer is introduced, the bulk impedance increases due to the resistance for lithium ion transport in the coating layer is larger than that in the liquid electrolyte in the needle-like pores [23]. The ion conductivity of the PP separator is $3.02 \times 10^{-4} \text{ S cm}^{-1}$. And the ion conductivity of the LAGP-PP is $2.67 \times 10^{-4} \text{ S cm}^{-1}$, which is higher than that of the AL-PP ($2.49 \times 10^{-4} \text{ S cm}^{-1}$).

The schematic diagram for the lithium ion diffusion in the ceramic coating layer is given in Fig. 4c. The higher ion conductivity of LAGP-PP demonstrates that the LAGP coating layer provides more facile lithium ion diffusion channels after being filled with liquid electrolyte. Since the Gurley values of LAGP-PP is lower than

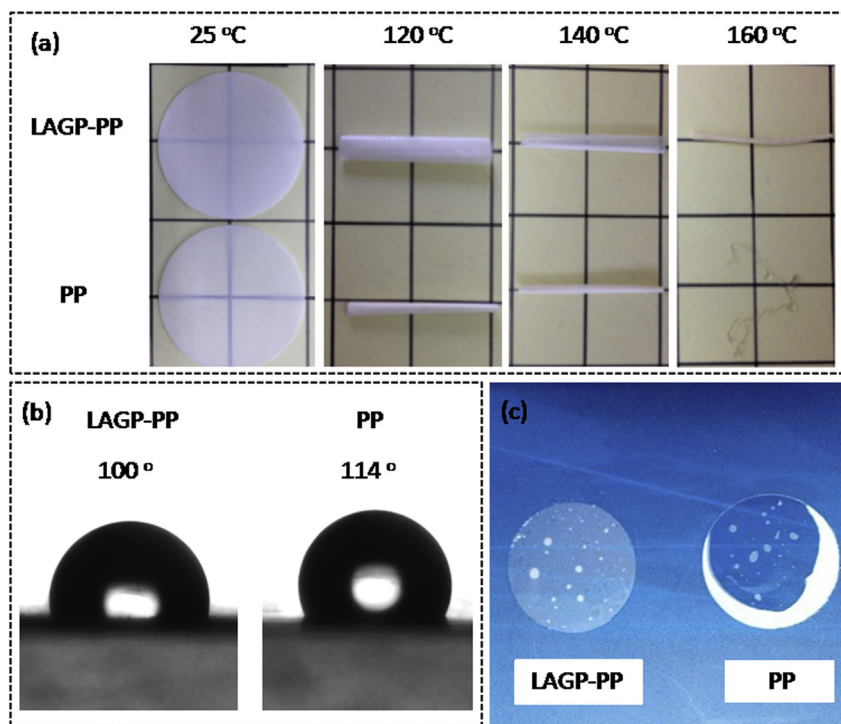


Fig. 3. (a) The thermal shrinkage of the LAGP-PP and PP separator after being treated at different temperature for 1 h. (b) The water contact angles of the LAGP-PP and PP separator. (c) The photograph of the wetting behavior of the separators with liquid electrolyte (S-3015A, 1 M LiPF_6 in a mixture of ethylene and dimethyl carbonate (3:7 vol ratio), Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd., China).

that of the AL-PP one. The contribution of the voids formed between the inorganic particles to the ion conductivity should be smaller for LAGP-PP separator due to the voids are the main pathway for lithium ion migration in the liquid electrolyte in the coating layer. However, the LAGP particles could also conduct lithium ions [19], so the diffusion resistance for lithium ions is smaller. While for the AL-PP separator, the transportation of lithium ions could only occur in the more tortuous paths between the particles, yielding lower ion conductivity.

The cycle performances were carried out between 3.0 V and 5.0 V with the assembly of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode/separator-liquid electrolyte/lithium anode. Fig. 5a shows the C-rate capacity of the cells containing PP, LAGP-PP and AL-PP separators. For the AL-PP separator, the discharge capacity shows a large decrease when the current rate rises. While the cells containing PP and LAGP-PP separator show better rate performances. The discrepancy comes from the mobility of the lithium ions in the cells. AL-PP separator owns lower ion conductivity (Fig. 4), so when the cells were cycles at higher current rate, especially at 5 C and 6 C, low migration ability limits the effective intercalation/de-intercalation of lithium ions in/from the electrodes, resulting in lower discharge capacity [24].

The C-rate capacities of the cells containing PP and LAGP-PP separator are almost equal, but that for LAGP-PP separator is

slightly higher. Although the bulk ion conductivity of the LAGP-PP separator is lower than that of the PP one, the enhanced wettability is deemed to give birth to a more uniformly wetted interfacial layer between the electrode and the separator, which helps to prevent the over-growth of the SEI film. A thinner and more compact SEI layer could be formed during the cycling process due to the strong affinity of the particles to the ionic species in the liquid electrolyte. Furthermore, these particles could prevent some unwanted reactions at the interfacial layer [25]. Therefore, the rate performances of the cells containing the LAGP-PP are better. The results clearly show the advantages of the LAGP coating layer over the inert inorganic one.

The cycling performances were further tested at 1 C/1 C charge/discharge current rate. As shown in Fig. 5b, the variation of the discharge capacity for the separators is similar with that of the C-rate capacity. The causes of the variation are as above. High ion conductivity and improved wettability contributes to better cyclability for the LAGP-PP separator [26].

The interfacial stability of the coin cells containing the PP, LAGP-PP and AL-PP separators was evaluated by comparing the changes of the interfacial resistances (R_{int}) before and after the cycling process. For battery formation, the coin cells were firstly cycled at 0.1 C for 3 times, and the initial R_{int} was recorded. Then after 100 cycles at 1 C, the final R_{int} of the coin cells was recorded. As shown

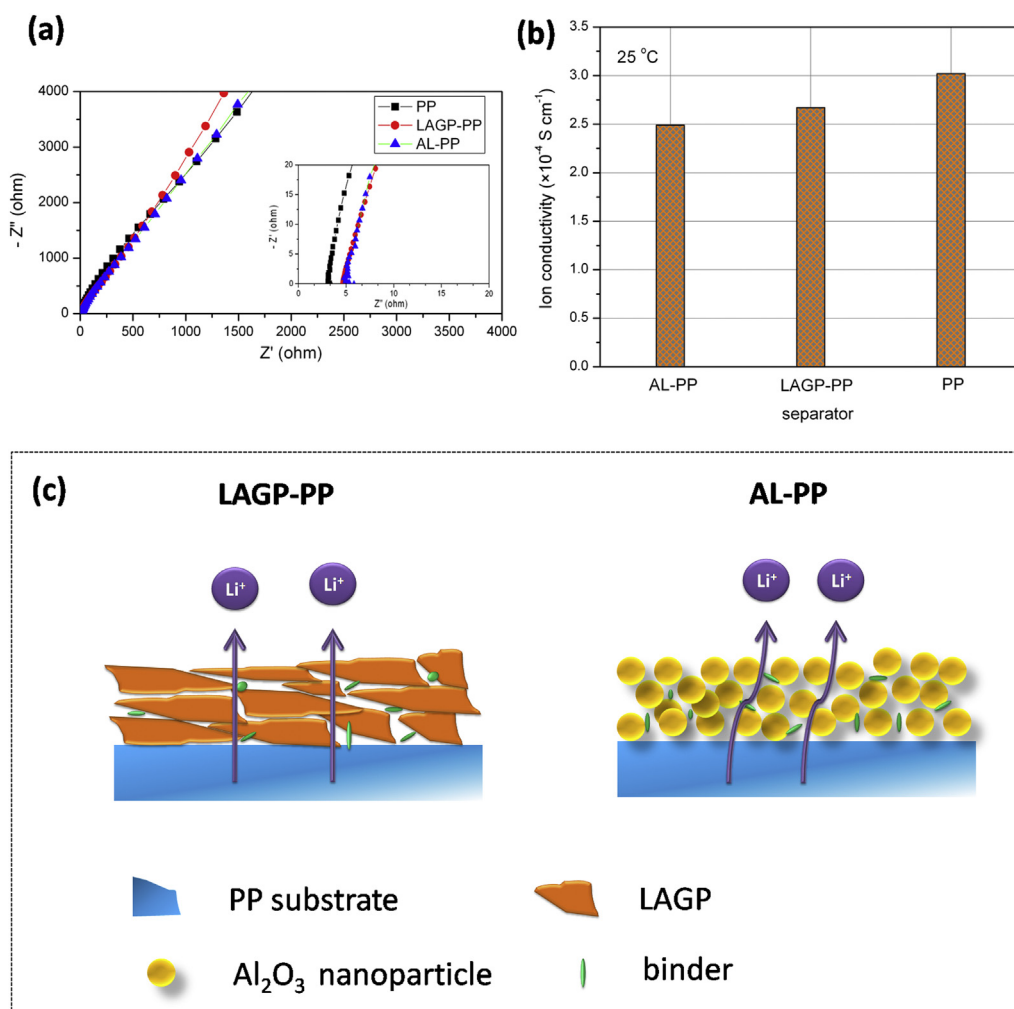


Fig. 4. (a) The Nyquist plots of PP, LAGP-PP, AL-PP separator. (b) The ion conductivity of the PP, LAGP-PP, AL-PP separator at 25 °C. (c) The schematic diagram of lithium ionic transport in the coating layer of LAGP-PP and AL-PP separators.

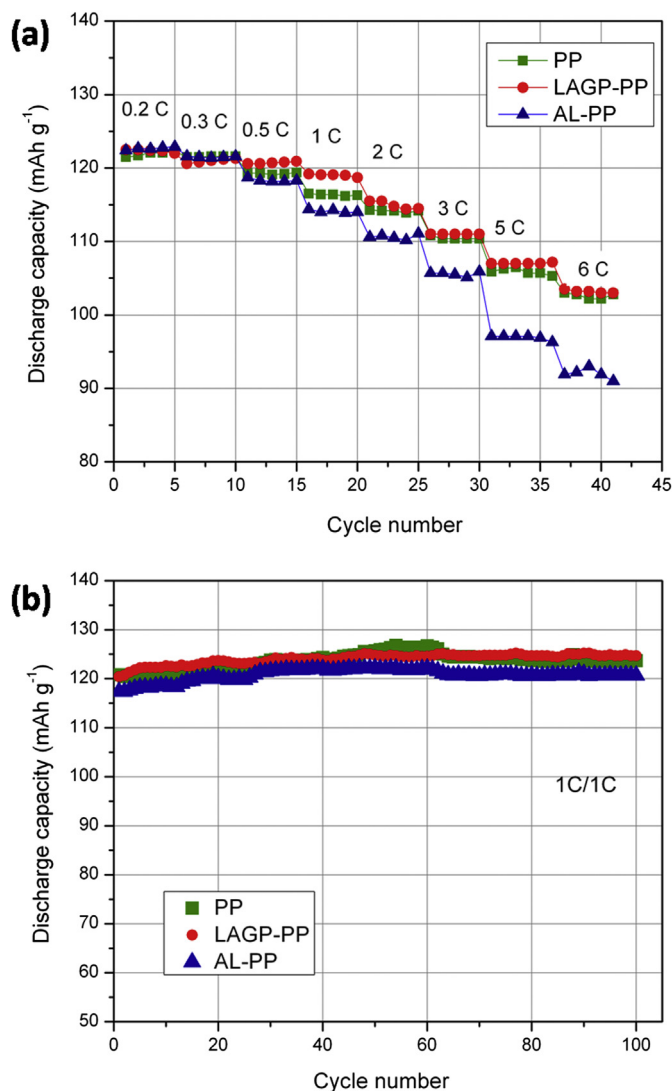


Fig. 5. (a) Comparison of the C-rate capacity (the charge current rate is 0.1 C). (b) The discharge capacity as a function of the cycle number (1 C/1 C).

in Fig. 6, the semi-circle in the Nyquist plots represents R_{int} . The initial R_{int} is 45, 75, 80 Ω for the coin cells with PP, LAGP-PP and AL-PP separator, respectively, which is believed to strongly depend on the mobility of lithium ions at the surface layer of the separator. As discussed above, since inorganic coating layer is introduced, the migration ability of lithium ions at the coating layer weakens. So R_{int} increases for cells containing the composite separators. Besides, due to the more facile lithium ion diffusion channels in the LAGP coating layer (Fig. 4c), the R_{int} for the cells containing the LAGP-PP separator is slightly higher than that containing the AL-PP separator.

R_{int} increases as the cycle number being increased. The reason is deemed to be the growth of the SEI film [9]. The changes of R_{int} for the coin cells containing the composite separators (Fig. 6) are much lower than that for the coin cells assembled with PP separator (55 Ω), which suggests that the inorganic coating layer is conducive to the interfacial stability of the batteries. The interfacial stability is found to be closely related to the wettability of the separators, because enhanced wettability could yield a more uniformly wetted and benign contact interfacial layer in the batteries, which could restrict the growth of the SEI film. The contact angle of the AL-PP separator is determined to be 92° (Table 1), lower than that for

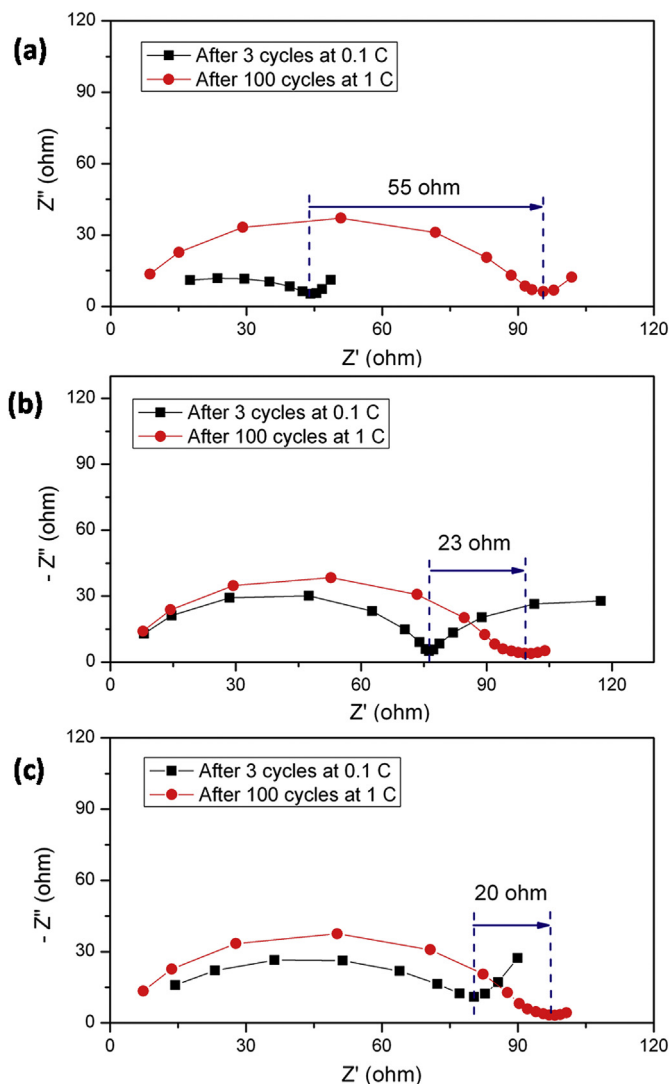


Fig. 6. Variations of the impedances of the coin cells containing (a) the PP separator, (b) LAGP-PP separator and (c) the AL-PP separator before and after 100 cycles.

the LAGP-PP separator (100°), indicating better wettability. So the R_{int} change for the AL-PP separator is smaller. However, after comprehensive comparisons, the LAGP-PP separator owns better electrochemical performances than the pristine PP one and the AL-PP one in the LiNi_{0.5}Mn_{1.5}O₄ based high-voltage lithium ion batteries.

4. Conclusions

Lithium ionic conducting glass ceramic LAGP is introduced onto the PP separator (LAGP-PP). The physical and electrochemical performances of the composite separator are investigated and compared with that of the pristine PP separator and the AL-PP separator. Thermal stability and wettability of LAGP-PP separator are effectively improved due to the introduction of LAGP. High ion conductivity and enhanced interfacial stability give birth to superior C-rate capacity and cyclability in the LiNi_{0.5}Mn_{1.5}O₄ based 5 V lithium ion batteries. In consideration of battery safety and cycle performances, the LAGP-PP separator is deemed to be an ideal candidate for the separators used in high voltage (5 V) high power lithium ion batteries.

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